

# Computational Study on the Dependence of Electronic Transition Energies of Porphin, Chlorin, Mg-Chlorin and Chlorophyll *a* on an External Charge

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In photosynthetic light harvesting complexes, the electronic transition energies of chlorophylls are influenced by the Coulombic interaction with nearby molecules. Variation of the interactions caused by structural inhomogeneity in biological environment results in a distribution of disordered electronic transition energies of chlorophylls. In order to provide a practical guide to predict qualitative tendency of such distribution, we model four porphyrin derivatives including chlorophyll *a* molecule interacting with an external positive charge and calculate their transition energies using the time dependent density functional method. It is found that  $\pi$ - $\pi^*$  transition energies of the molecules are generally blue-shifted by the charge because this stabilizes occupied molecular orbitals to a greater extent than unoccupied ones. Furthermore, new transitions in the visible region emerge as a result of the red-shift in energy of an unoccupied Mg orbital and it is suggested that light-induced electron transfer may occur from the tetrapyrrole ring to the central magnesium when the molecules are interacting with a positive charge.

**Key Words** : Charge dependence, Electronic transition, Chlorophyll *a*, DFT, Disorder

## Introduction

Porphyrin derivatives (especially chlorophyll molecules) play an important role in energy transformation processes occurring in biological systems and have therefore been the subject of many experimental<sup>1-4</sup> and theoretical<sup>5-8</sup> studies. Photosynthetic apparatus in Nature stores solar energy by absorbing it via electronic transitions of such molecules. The absorbed energy is transferred to other chlorophyll (Chl) molecules and finally used as the energy source for electron transfer reactions leading to the synthesis of carbohydrates. For the study of molecular details of such processes, information about the electronic structure of the Chl molecules is essential.<sup>9</sup>

Electronic energies of the molecules in biological systems are influenced by their local environments such as hydrogen bonding, Coulombic interaction with charged residues of backbone proteins, interaction with a ligand.<sup>10</sup> The local environment varies from a molecule to another and, as a result, the electronic transition energies of chromophore molecules in biological systems should be widely disordered. Such disordered transition energies affect the mechanism of the energy transfer in photosynthetic systems.<sup>11</sup> Therefore it may be useful to provide a practical guide how the electronic transition energies of Chl molecules are influenced by the factors mentioned above. In this paper, we investigate the influences of a positive point charge on electronic transition energy, oscillator strength, and molecular orbitals of a few porphyrin derivatives including Chl *a* molecule.

The visible part of electronic structures of porphyrin derivatives is often explained in terms of the four-orbital model suggested by Gouterman.<sup>12,13</sup> In the model, only four

frontier molecular orbitals (two highest occupied molecular orbitals (HOMO) and two lowest unoccupied molecular orbitals (LUMO) of the conjugated  $\pi$ -electrons in tetrapyrrole ring are considered for the interpretation of electronic transitions in visible region. Within this model, four singly excited configurations are constructed. Linear combinations of these four configurations form four bands of electronic transition from the ground state which are called  $Q_x$ ,  $Q_y$ ,  $B_x$ , and  $B_y$  bands.

Electronic spectra of porphyrin derivatives have been theoretically studied by semi-empirical calculation methods,<sup>14,15</sup> time-dependent density functional theory (TD-DFT),<sup>16,17</sup> and *ab initio* methods.<sup>18-20</sup> In a series of study performed by Sundholm,<sup>21-24</sup> it was shown that TD-DFT should give the most accurate results on the electronic transition energy of the porphyrin derivatives. Therefore we will employ TD-DFT for the calculations of electronic excited states in the present paper.

## Computational Methods

We consider four porphyrin derivatives, porphin, chlorin, magnesium-chlorin (Mg-chlorin), and Chl *a* the structures of which are shown in Figure 1. Porphin is the most fundamental molecule of macrocyclic tetrapyrrolic ring systems and we included this molecule in our study because we can learn the basic electronic structure of the other molecules. The phytol chain of Chl *a* does not significantly affect the electronic transition energy of the  $\pi$ -electrons in the tetrapyrrolic ring<sup>22</sup> (which is responsible for the visible region of the electronic transitions of the molecules) and therefore we replaced it by a hydrogen atom. The simplest metallo-

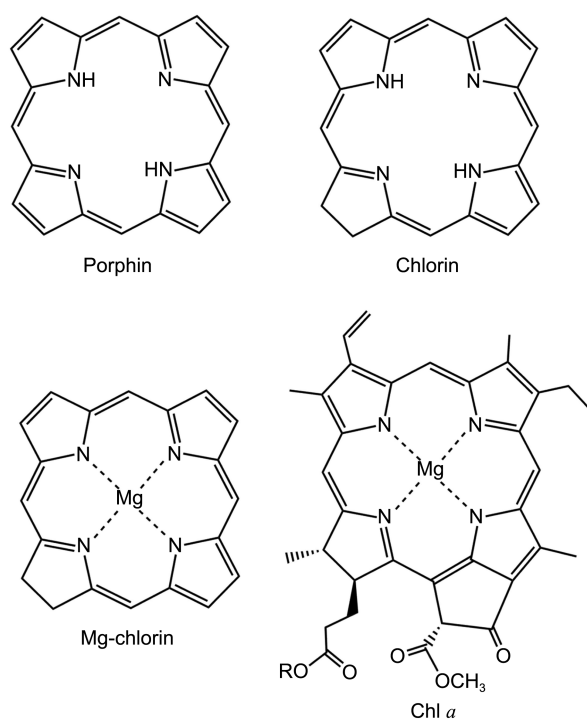


Figure 1. Molecular structures of four porphyrin derivatives.

chlorin, Mg-chlorin, consists of a magnesium atom ligated by four nitrogen atoms of the tetrapyrrolic ring. The geo-

metries of the molecules in their ground electronic states were optimized using the density functional method with the Becke exchange functional (Becke88)<sup>25</sup> and 6-31G basis set. All the calculations for electronic transition energies were performed on the optimized geometries. In order to examine the influence of a point charge on the electronic excited states, we put a positive point charge at a few points in a vertical distance of 3.5 Å on top of the ring plane. This value is a typical distance, which is found from X-ray crystal structures of biological light harvesting complexes, from the metal atom of a chlorophyll molecule to ligand residue supporting it.

We calculated electronic transition energies using TD-DFT method with the Becke 88 functional which has been extensively implemented to study UV/vis absorption spectra of chlorophyll molecules<sup>21,22</sup> and free-base porphyrin.<sup>23</sup> Those studies showed a one-to-one correspondence between the calculated excitation energies and the measured absorption maxima. Based on these findings, we employed the same density functional in the present paper. Dependence of the energies on basis sets is examined by calculating the transition energies from the ground state to a few excited states of each molecule with three levels of Pople basis sets, 3-21G\*, 6-31G, and 6-31G\*.<sup>26,27</sup> Since this paper does not intend to provide quantitative analysis but to present qualitative tendency in the behavior of electronic transitions, we decided not to employ higher levels of basis set which

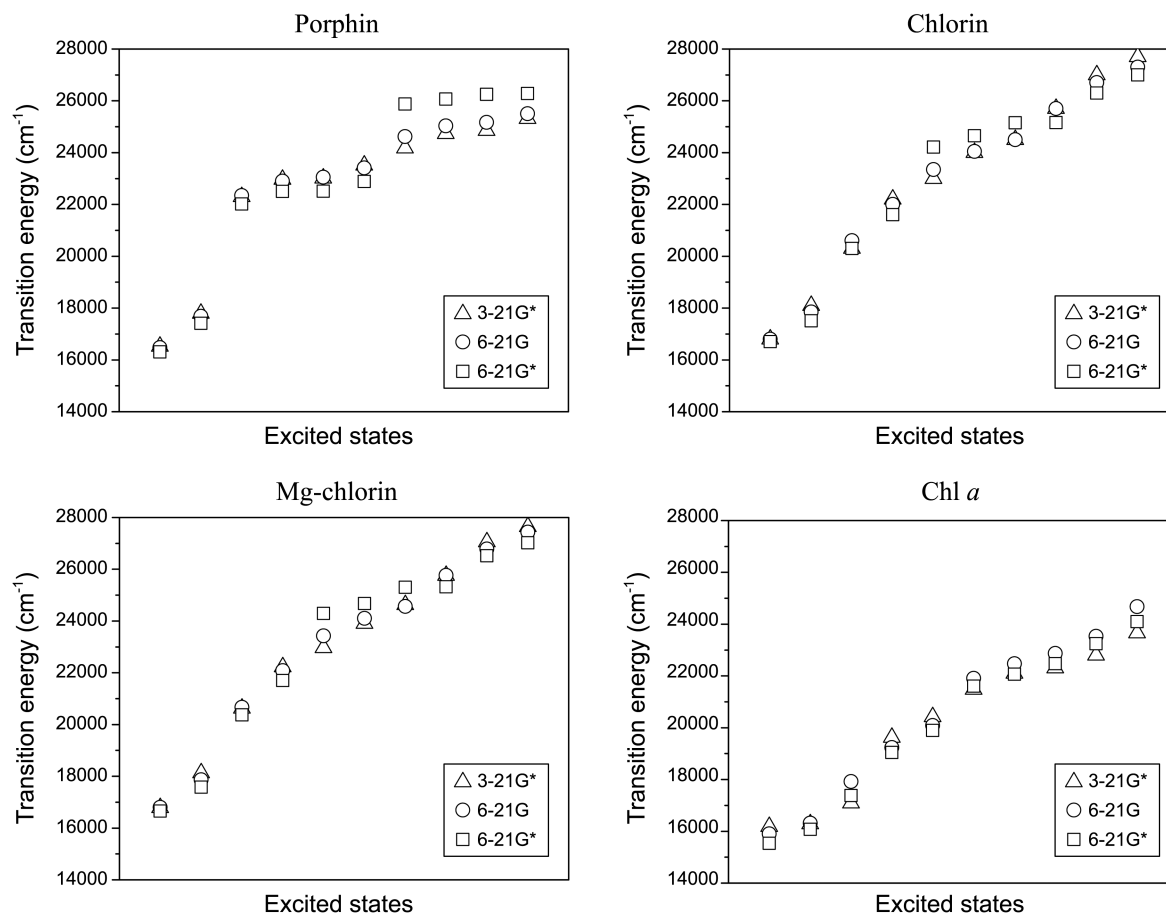


Figure 2. Dependence of calculated electronic transition energies on basis set.

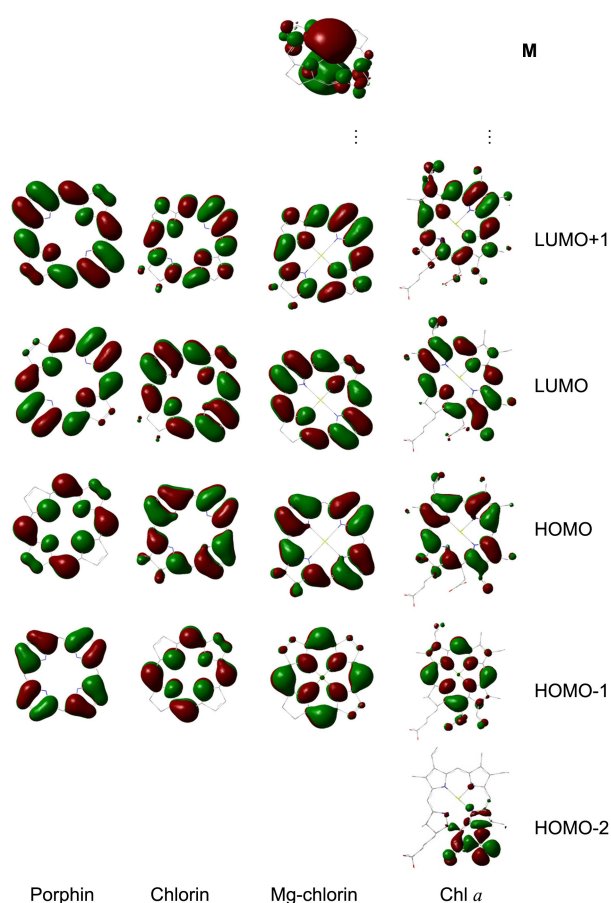


Figure 3. Shapes of molecular orbitals.

require expensive computations. As we can see in Figure 2, the transition energies to Q-bands (S1 and S2 states) are found not to be very sensitive to the basis sets. Based on this observation, we used TD-DFT/Becke88/6-31G method in the further computations. Quantum chemical package used in the present work was Gaussian 03 parallelized using LINDA on a clustered intel xeon computers.<sup>28</sup>

## Results and Discussion

**Molecular Orbital Shape and Electronic Transition Energy.** The shapes and energies of molecular orbitals (MOs) in the vicinity of the frontier orbitals of the four molecules are shown, respectively, in Figure 3 and 4. As we expect, the shapes are very similar over the four molecules and the MOs include  $\pi$ -electrons of the tetrapyrrolic ring. The HOMO energy of each molecule is set to zero and Figure 4 shows the relative MO energies to it. We note that the highest state of Mg-chlorin in Figure 4 corresponds to the unoccupied  $4p$  atomic orbital of the central magnesium denoted by M in Figure 3. Chl *a* also contains a central magnesium and the energy of Mg atomic orbital in Chl *a* (which is not displayed) was calculated to be similar in Mg-chlorin.

Table 1 presents the mixing coefficient of configuration interactions (CI), transition energies in wave number, and

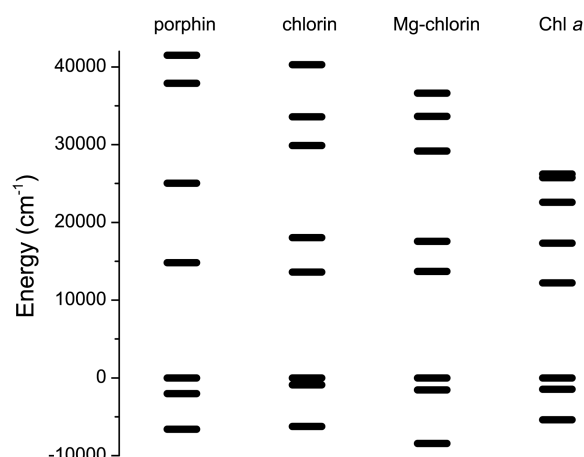


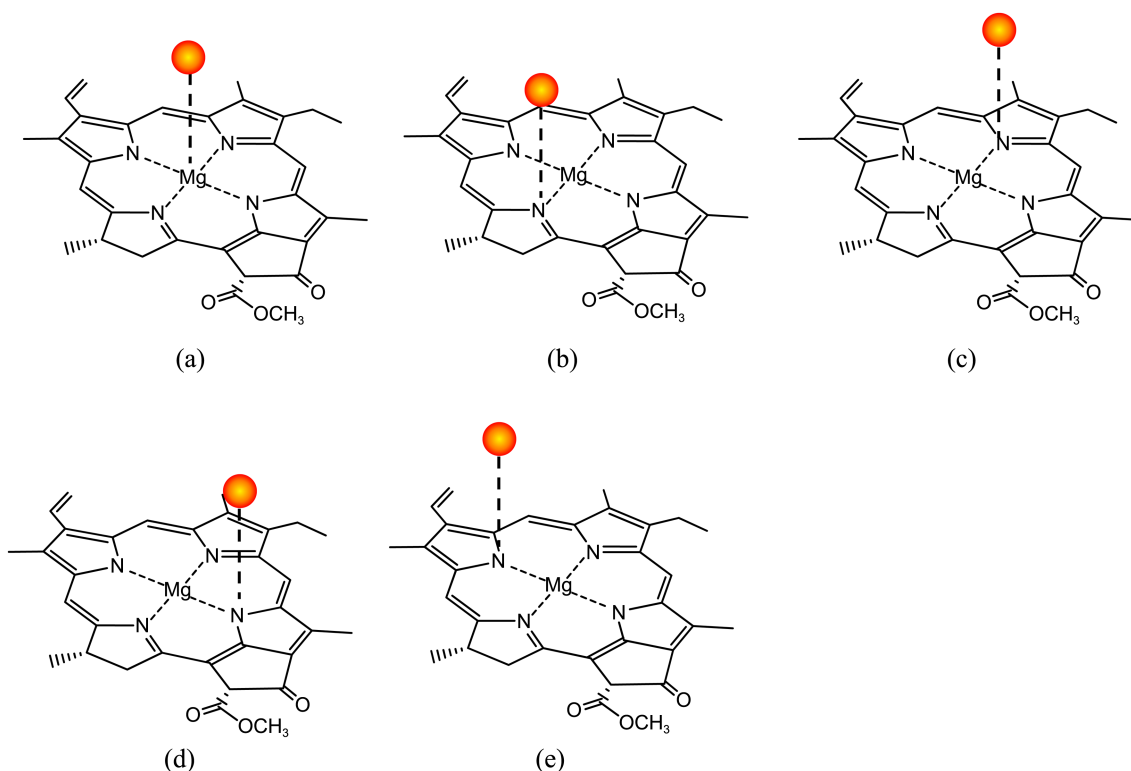
Figure 4. Relative energies of MOs in each molecule. HOMO energy of each molecule is set to be zero.

oscillator strengths for the transitions from the ground state to S1 and S2 states. The configurations with mixing coefficients less than 0.2 are not shown. Energy difference between S1 and S2 states ranges from 300  $\text{cm}^{-1}$  for Mg-chlorin to 1200  $\text{cm}^{-1}$  for porphin. For porphin and chlorin, S1 transition consists mainly of (HOMO-1)-to-(LUMO) and (HOMO)-to-(LUMO+1) transitions and S2 transition consists mainly of (HOMO-1)-to-(LUMO+1) and (HOMO)-to-(LUMO) transitions. For Mg-chlorin and Chl *a* which contain a magnesium atom, S1 transition consists mainly of (HOMO-1)-to-(LUMO+1) and (HOMO)-to-(LUMO) transitions and S2 transition consists mainly of (HOMO-1)-to-(LUMO)

Table 1. Mixing coefficient in CI, transition energy from ground state, and oscillator strength for the transitions to S1 and S2 states of isolated molecules in the absence of external charge. Experimental values are given in parentheses

	Molecule	CI	Energy ( $\text{cm}^{-1}$ )	Oscillator Strength
S1	Porphin	-0.43  H-1→L>	16473	0.0017
		+0.54  H→L+1>	(15970) <sup>a</sup>	(0.02) <sup>a</sup>
	Chlorin	+0.55  H-1→L>	16800	0.0111
		+0.38  H→L+1>	(15686) <sup>b</sup>	
	Mg-chlorin	+0.37  H-1→L+1>	17427	0.0754
	+0.53  H→L>	(16393) <sup>b</sup>		
S2	Chl <i>a</i>	-0.31  H-1→L+1>	15903	0.1636
		+0.56  H→L>	(15163) <sup>c</sup>	(0.23) <sup>c</sup>
	Porphin	+0.44  H-1→L+1>	17684	0.05
		+0.49  H→L>	(19519) <sup>a</sup>	(0.07) <sup>a</sup>
	Chlorin	-0.35  H-1→L+1>	17868	0.0940
+0.53  H→L>		(16393) <sup>b</sup>		
Mg-chlorin	+0.50  H-1→L>	17767	0.0036	
	-0.44  H→L+1>	(17406) <sup>b</sup>		
Chl <i>a</i>	+0.55  H-1→L>	16312	0.0229	
	+0.34  H→L+1>	(17421) <sup>c</sup>		

<sup>a</sup>In gas phase, see refs. 30 and 23. <sup>b</sup>In benzene, see ref. 31. <sup>c</sup>In ether, see refs. 32 and 24.



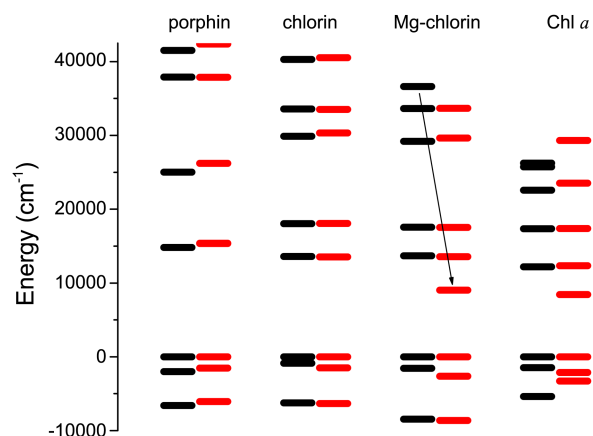
**Figure 5.** Five locations for a point charge on Chl *a*. (a) Vertical position separated by 3.5 Å from the center of tetrapyrrolic ring. (b)-(e) Vertical position separated by 3.5 Å from the nitrogen atom of pyrrolic ring.

and (HOMO)-to-(LUMO+1) transitions. In all cases, the transitions to S1 and S2 states correspond to  $\pi$ - $\pi^*$  transition involving the  $\pi$ -electrons fully delocalized over the tetrapyrrolic ring. Transition energies to S1 and S2 states predicted by the present computational methods reasonably agree with those observed in experiments (see Table 1).

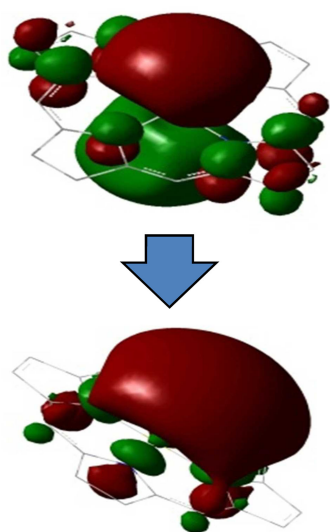
**Influence of a Point Charge on Molecular Orbitals.** In order to examine the influence of a point charge on the electronic transitions of the molecules, we chose five locations on top of the tetrapyrrolic ring where we put a positive point charge. Those locations are displayed in Figure 5. The vertical distance from the tetrapyrrolic ring plane to the point charge is set to 3.5 Å as discussed in Computational Methods.

First, we put the charge at the center of tetrapyrrolic ring as shown in (a) of Figure 5. This location is the nearest point to the central magnesium atom in Mg-chlorin and Chl *a* molecules and in this case the interaction between the point charge and metal atom is maximized for the given vertical separation distance. The energies of the MOs influenced by the point charge are shown in Figure 6. Due to the Coulombic interaction with the positive charge, the molecular orbitals are, on the whole, stabilized in some degrees. Extent of the stabilization in porphin and chlorin, not containing a Mg atom, is more or less similar over the MOs and therefore, in those molecules, relative energies of the MOs do not change significantly by the presence of the point charge. However, in Mg-chlorin and Chl *a* which contain a Mg atom, the vacant atomic orbitals of the metal protrude from the tetrapyrrolic ring and strongly interact with the point

charge. Therefore the molecular orbital M becomes much more stabilized than other MOs by the point charge being shifted down to below LUMO as shown in Figure 6 (With the charge, M becomes the lowest unoccupied molecular orbital but, for the purpose of comparison, in this paper LUMO indicates the MO corresponding to the lowest unoccupied molecular orbital formed *in the absence of the*

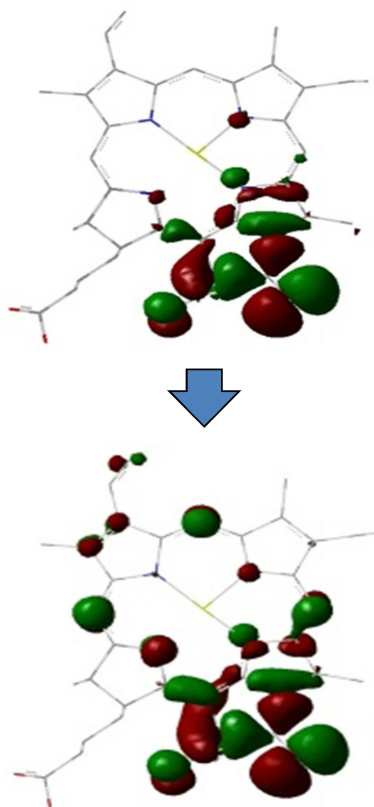


**Figure 6.** Energy diagram of molecular orbitals. In each molecule, the left diagram is for isolated molecule and the right diagram is for the same molecule interacting with a positive point charge located at the position shown in Figure 5(a). In Mg-chlorin and Chl *a*, the unoccupied 4p orbital of Mg protrudes over the tetrapyrrolic ring plane and interacts strongly with the point charge. This favorable interaction stabilizes the molecular orbital M as dictated by arrow.

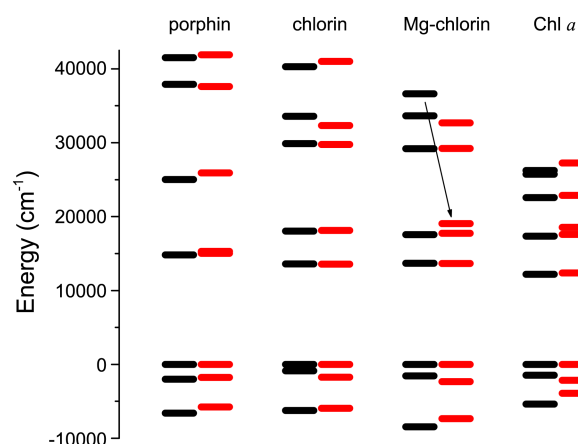


**Figure 7.** Molecular orbital M in mixing with the unoccupied 4p orbital of Mg. Top: in isolated Mg-chlorin. Bottom: in Mg-chlorin interacting with a positive charge located at the position shown in Figure 5(a).

charge). In addition, being pulled by the positive charge, the shape of M becomes asymmetric as shown in Figure 7. However, other MOs not mixed with the atomic orbital of Mg do not change noticeably in shape due to the point charge as illustrated in Figure 8 for HOMO–2.



**Figure 8.** Shape of HOMO–2. Top: in isolated Chl *a*. Bottom: in Chl *a* interacting with a positive charge located at the position shown in Figure 5(a).



**Figure 9.** Energy diagram of molecular orbitals. In each molecule, the left diagram is for isolated molecule and the right diagram is for the same molecule interacting with a positive point charge located at the position shown in Figure 5(b). In Mg-chlorin and Chl *a*, the unoccupied 4p orbital of Mg protrudes over the tetrapyrrolic ring plane and interacts strongly with the point charge. This favorable interaction stabilizes the molecular orbital M as dictated by arrow.

Next, we put the point charge at the vertical position above the nitrogen atom of a pyrrolic ring as shown in Figure 5(b). The vertical distance from the nitrogen atom to the point charge is the same as before, 3.5 Å. The energies of the MOs affected by the point charge at this location are shown in Figure 9. Similarly to the previous case, the energies of the MOs in the molecules not containing metal atom are not significantly affected by the charge but the orbital M in metal-containing molecules is much stabilized by the point charge. However, the stabilization energy in this case is less than the stabilization energy when the charge is located on top of the metal atom. This is because the separation distance between the point charge and metal atom increases in Figure 5(b) and consequently the interaction strength becomes weaker. Although the stabilization energy is substantially reduced from the case in Figure 6, the change in shape of the orbital M is found to be similar to what is shown in Figure 7. Therefore we conclude that the molecular orbital M is strongly influenced in energy and in shape by the presence of external charge. But the detailed lateral location does not much matter with the influence on molecular orbital shape. We performed the same calculations for the other three locations of point charge shown in Figure 5 and obtained similar results.

**Influence of a Point Charge on Electronic Transition Energy.** Since the MO energies are affected by the external point charge, the electronic transition energies from the ground state to S1 or S2 states should be shifted in a certain extent. The shifts in transition energies are summarized in Table 2 [for the charge located as in Fig. 5(a)] and Table 3 [for the charge located as in Fig. 5(b)]. Although all MOs are stabilized by the positive point charge, the stabilization energy is found to be generally greater in the occupied MOs than in the unoccupied MOs with an exception of the orbital M. This seems to be so because the electron population

**Table 2.** Mixing coefficient in CI, transition energy shift, and oscillator strength for the transitions to S1 and S2 states of the molecules when a positive charge is located on top of the center of the tetrapyrrolic ring as shown in Figure 5(a). Energy shift is the amount of transition energy shifted by the coupling to the point charge

	Molecule	CI	Energy Shift (cm <sup>-1</sup> )	Oscillator Strength
S1	Porphin	+0.44  H-1→L>	332	0.0010
		+0.53  H→L+1>		
	Chlorin	+0.54  H-1→L>	376	0.0086
		+0.39  H→L+1>		
	Mg-chlorin	-0.25  H-1→L+1>	-233	0.0623
		+0.52  H→L>		
+0.3  H-3→M>				
Chl <i>a</i>	+0.37  H-4→M>	434	0.1200	
	-0.26  H-1→L+1>			
	+0.42  H→L>			
S2	Porphin	-0.45  H-1→L+1>	313	0.0001
		+0.49  H→L>		
	Chlorin	-0.33  H-1→L+1>	115	0.1038
		+0.54  H→L>		
	Mg-chlorin	+0.50  H-1→L>	419	0.0010
		+0.45  H→L+1>		
+0.35  H-2→L>				
Chl <i>a</i>	+0.42  H-1→L>	757	0.0182	
	+0.37  H→L+1>			
	+0.37  H→L+1>			

inside the tetrapyrrolic ring is a little greater in occupied MOs than in unoccupied MOs as we can see in Figure 3. Consequently, favorable interaction with the external point charge located at the central area of the tetrapyrrolic ring (where protein residue ligands in biological systems are located) is stronger for the occupied MOs and leads to more energy of stabilization. As a result, the transition energies from the ground state to S1 or S2 states are generally blue-shifted by the interaction with a positive external charge. If the external charge is negative, we expect the transition energy should be red-shifted because the negative charge will destabilize the occupied MOs in a greater extent.

First we discuss Table 2 which is for the case of the point charge located at the center of tetrapyrrolic ring. In porphin and chlorin which do not contain a central Mg atom, the main contributions to the transition to S1 state come from (HOMO-1)-to-(LUMO) and (HOMO)-to-(LUMO+1) transitions in a similar way to when there is no point charge. On the while, the transition energies are blue-shifted by the interaction with the charge by 332 cm<sup>-1</sup> for porphin and 376 cm<sup>-1</sup> for chlorin as discussed above. Although the fact that the main contributions to the transition to S2 state come from (HOMO-1)-to-(LUMO+1) and (HOMO)-to-(LUMO) transitions also does not change by the presence of the external charge, the transition energies are blue-shifted by 313 cm<sup>-1</sup> and 115 cm<sup>-1</sup>, respectively, for porphin and chlorin.

In contrast with the non-metallic chromophores, the metal-

**Table 3.** Mixing coefficient in CI, transition energy shift, and oscillator strength for the transitions to S1 and S2 states of the molecules when a positive charge is located on top of nitrogen atom as shown in Figure 5(b). Energy shift is the amount of transition energy shifted by the coupling to the point charge

	Molecule	CI	Energy Shift (cm <sup>-1</sup> )	Oscillator Strength
S1	Porphin	-0.42  H-1→L>	226	0.0008
		+0.53  H→L+1>		
	Chlorin	+0.55  H-1→L>	446	0.0064
		+0.39  H→L+1>		
	Mg-chlorin	+0.35  H-1→L+1>	174	0.0878
		+0.54  H→L>		
Chl <i>a</i>	+0.29  H-1→L+1>	223	0.1503	
	+0.54  H→L>			
S2	Porphin	+0.44  H-1→L+1>	186	0.0008
		+0.49  H→L>		
	Chlorin	-0.33  H-1→L+1>	232	0.1130
		+0.54  H→L>		
	Mg-chlorin	+0.50  H-1→L>	399	0.0019
		-0.45  H→L+1>		
Chl <i>a</i>	+0.38  H-2→L>	857	0.0144	
	+0.40  H-1→L>			
	-0.35  H→L+1>			

containing molecules show significant changes in energy and shape of the MOs as well as in transition energies to S1 and S2 states upon interacting with the external charge. As we can see in the mixing coefficient for the configuration interaction, in the presence of the external positive charge, the orbital M is lowered in energy and consequently makes substantial contributions to the transitions to S1 and S2 states. Then the electronic transitions to S1 and S2 states should result in electron transfer from  $\pi$  orbitals of tetrapyrrolic ring to the atomic orbital of the central Mg atom. The transition energies are changed in an unexpected way by the point charge. In Mg-chlorin, the transition energy is red-shifted by the charge in contrast with what we have seen in non-metallic derivatives. This is because the unoccupied orbital M is largely stabilized by the interaction with the charge and then makes a contribution to the transitions to S1 and S2 states.

The transition energies of Chl *a*, another metal-containing molecule, are found to behave differently; those are blue-shifted by 434 cm<sup>-1</sup> similarly to what is found in the non-metallic molecules. This is because, in spite of the large stabilization of the orbital M, it is coupled by HOMO-4 in the configuration interaction the energy of which is much lower than HOMO-1 and so the transition energy is blue-shifted.

In Table 3, the shifts in transition energies to S1 and S2 states when a point charge is located above the nitrogen atom [see Fig. 5(b)] are displayed. In this case, the interaction strength between the charge and molecules are weaker as discussed above and the stabilization energy of the orbital M

is not as great as in the previous case and this MO does not play a significant role in the transitions to S1 and S2 states. Therefore the transition energies are generally blue-shifted by the same reason as in non-metallic molecules. On the while, we found that a few new transitions whose transition wave length is in the range of 500-700 nm appear as a result of the interaction with the point charge. This may lead to a broadening mechanism of absorption spectra in biological systems.

As discussed above, in the two molecules containing a central Mg atom, the shift in transition energy by the interaction with an external charge behave in a complicated way depending on the characteristics of molecular orbitals associated with the transition. Therefore it may not be possible to predict how an external charge influences the transition energy in terms of simple classical arguments. Rather, accurate quantum chemical calculations with detailed information of molecular structure should be performed.<sup>29</sup>

### Summary

In order to understand the diversity in electronic transition energy of the chlorophyll molecules in biological light harvesting complexes, we studied model systems of four porphyrin derivatives, porphin, chlorin, Mg-chlorin, and Chl *a* interacting with an external positive point charge located above the tetrapyrrolic ring plane. We calculated molecular orbitals and electronic transition energies to S1 and S2 states for the four molecules interacting with the point charge by using TD-DFT method. The transition energies calculated by the same computational method in the absence of the charge are in reasonably good correlation to experimental data and then we examined the quantum chemical characteristics of electronic transitions of the porphyrin derivatives influenced by the external point charge.

The transition energies of non-metallic derivatives are found to be generally blue-shifted by the interaction with an external positive charge due to stabilization of occupied molecular orbitals. In metal-containing derivatives, Mg-chlorin and Chl *a*, the atomic orbital of the central Mg atom has been found to play an important role in electronic transition in the presence of an external charge. Due to the strong interaction of the atomic orbital with the charge, the molecular orbital in mixing with the atomic orbital is much stabilized by the presence of nearby positive charges and then the transition energy to S1 state can be red-shifted or blue-shifted from that of isolated molecules depending on the detailed location of the external charge. Furthermore, a few new transition bands have been shown to emerge as a result of the interaction with the charge. This may lead to a

broadening mechanism of absorption line shape of chlorophyll molecules in biological environments where various distributions of external charges are often found.

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